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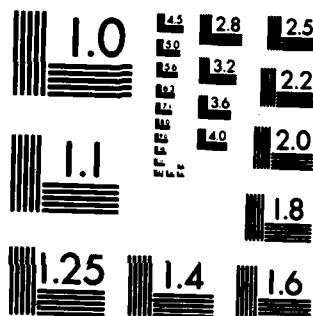
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POTENTIODYNAMIC POLARIZATION STUDIES OF AN Al-Mg-Li ALLOY

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Troy, New York 12181

April 1983

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13. ABSTRACT Potentiodynamic polarization tests were compared for an Al-Mg-Li alloy and a 7000 series alloy (7050). Tests were performed in various concentrations of sodium chloride, sodium sulfate and sodium nitrate solutions as functions of scan rate, pH, temperature, and degree of aeration. The lithium containing alloy exhibited significantly more active corrosion potentials in neutral and acidic solutions while the pitting potentials were essentially the same for the two alloys.		

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POTENTIODYNAMIC POLARIZATION STUDIES OF AN Al-Mg-Li ALLOY

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Potentiodynamic polarization tests were compared for an Al-Mg-Li alloy and a 7000 series alloy (7050). Tests were performed in various concentrations of sodium chloride, sodium sulfate and sodium nitrate solutions as functions of scan rate, pH, temperature, and degree of aeration. The lithium containing alloy exhibited significantly more active corrosion potentials in neutral and acidic solutions while the pitting potentials were essentially the same for the two alloys.



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Introduction

Lithium containing alloys of aluminum are promising alternatives to either existing alloys or composites. The combined reduction in density and increases in strength and elastic modulus has attracted much interest in this system. However, most of the alloys developed to date have not been placed in service due to poor fracture toughness. If alloys are developed with improved fracture toughness, then the corrosion behavior of these alloys will be of great interest.

Aluminum is an active metal ($E^\circ=1.71$ V vs. she) and derives its corrosion resistance from an adherent continuous passive film of oxides or hydroxides (1). As a result, the corrosion behavior of aluminum and its alloys is completely determined by the stability of this layer and the rate at which it reforms when ruptured (2).

Lithium is a very active element ($E^\circ=3.05$ V vs. she) and therefore could have dramatic effects on the corrosion properties of an alloy even in small concentrations. Niskanen et. al. studied the effect of heat treatment and microstructure on the corrosion of various Al-Li-X alloys (3,4). They found that overaging, resulting in the precipitation of the equilibrium phase AlLi, had a deleterious effect on the corrosion properties of the alloys studied. However, in the Al-Li-Mg alloys the formation of Al_2MgLi prevented the formation of the anodic AlLi phase and resulted in improved corrosion properties. A similar study on an Al-Li-Cu-Mg alloy also showed no deleterious effect of overaging (5).

This program was undertaken to determine the corrosion properties of an Al-Mg-Li alloy in a variety of environments under a variety of environmental and electrochemical conditions and to compare the behavior of the lithium containing alloy to the behavior of a normal 7000 series alloy (7050).

Materials and Procedures

Two alloys were chosen for this study. The first was an Al-Mg-Li alloy and the second was an alloy of the 7000 series (7050). The lithium containing alloy was supplied by the Naval Air Development Center, Warminster PA and the 7050 alloy was supplied by Alcoa Pittsburgh PA. The compositions of the alloys are shown in table I.

Cylindrical samples were machined from each of the alloys. The samples were then ground with successively finer grades of silicon carbide papers to 600 grit and then polished with 9 micron diamond paste. Samples were reconditioned after each test machining off the exposed surface and then repeating the procedure above to produce a fresh surface for each test.

Tests were performed in a standard glass polarization cell with the sample mounted on a steel rod encased in glass and sealed with a teflon gasket as shown in figure 1 (6). Only the totally immersed sample, teflon gasket and glass made contact with the solution. Potentials were measured with a Luggin capillary and a saturated calomel electrode and all reported voltages are verses the saturated calomel electrode (0.0 V

Table I. Chemical Analysis of Alloy Composition

Element	7050 Alloy	Al-Mg-Li Alloy
Mg	2.41	4.24
Zn	6.52	0.004
Li	- -	2.13
Cu	2.20	0.030
Zr	0.113	- -
Cr	0.029	<0.002
Fe	0.147	0.01
Si	0.109	0.10
Ti	0.050	<0.005
Al	Rem.	Rem.

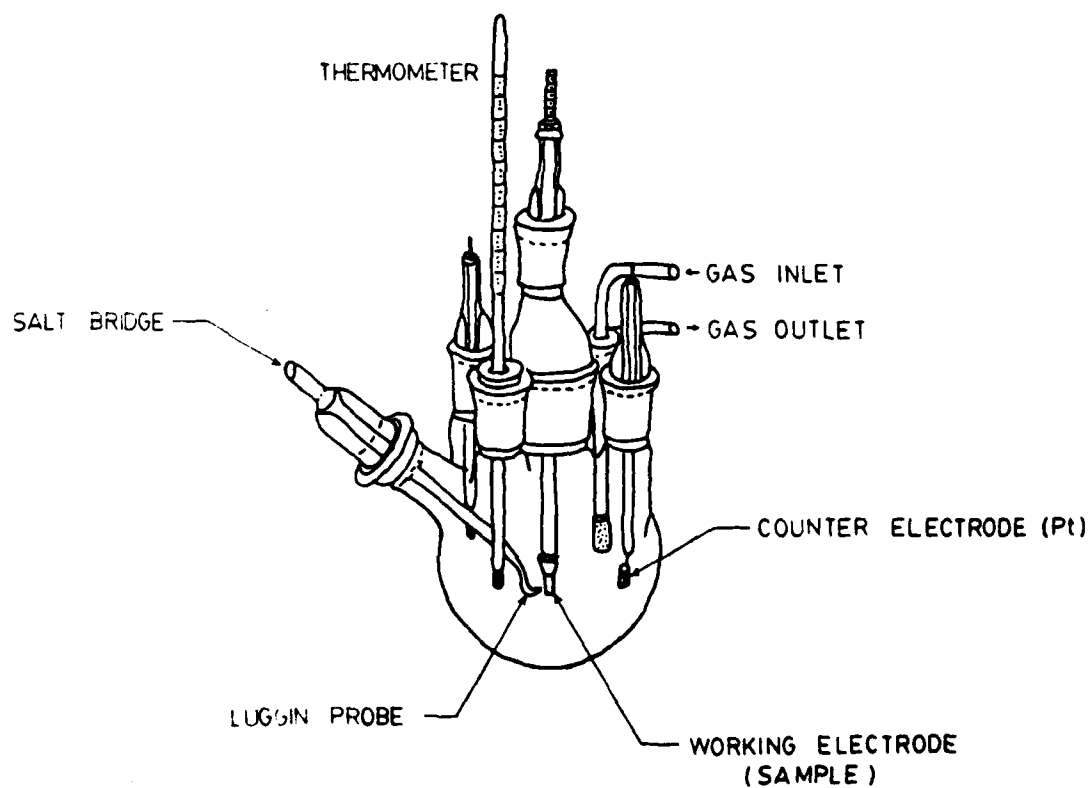


Figure 1. Diagram of a typical polarization cell.

vs. sce = 0.242 V vs. she). Temperatures were maintained constant utilizing a temperature bath filled with water into which the corrosion cell was immersed. The temperature of the solution in the cell was monitored with a standard laboratory thermometer.

All solutions were mixed, thoroughly deaerated and stored under nitrogen prior to use. The solutions were then deaerated with nitrogen or aerated with air for at least one hour prior to insertion of the sample. Bubbling of either nitrogen or air was continued for the duration of the tests to maintain conditions and to agitate the solutions.

The samples were inserted into the solutions for a period of 30 minutes to reach the steady state or free corrosion potential. Monitoring of the potential during this period and for longer durations indicated that this potential was reached in 10 to 20 minutes. A dynamic potential scan was started at a potential 100 mV active to the corrosion potential and continued to a potential sufficiently noble to cause pitting prior to reversing the scan. If pitting did not occur the scan was halted manually. The scans shown in the figures are active to noble potential scans. The reverse scans usually retraced the original scan.

Results

Scan Rate

Figure 2 shows the effect of scan rate on the measured pitting and corrosion potentials of the alloys. The slower scan rate resulted in reproducibly lower current densities at a given potential, indicating that the achievement of a steady state passive film is time dependent. That is, the steady state thickness of the passive layer increases with increasingly noble potentials and film growth is time dependent. However, figure 2 shows that the pitting potential is not significantly altered by the increased scan rate.

Aeration

Aeration of the solutions reduced the passive current density and increased the free corrosion potential of the alloys in the environments tested. The pitting potentials are essentially unchanged. Figure 3 shows the effect of aeration on the Al-Mg-Li alloy in 0.5 N sodium chloride. In the 7050 alloy this resulted in pitting either during the 30 minute exposure before the test or on passing the zero potential during the scan. The Al-Mg-Li alloys free corrosion potential also increased but not enough to result in pitting. Table II lists the results of aeration tests compared to deaerated tests for sodium chloride solutions with varying pH.

pH

Increasing the pH of the solution reduces the corrosion potential of both alloys while not significantly altering the pitting potential for a fixed chloride ion concentration and temperature. The free corrosion potential for the alloys in 0.5 N sodium chloride of pH 10, table II, are similar. They are

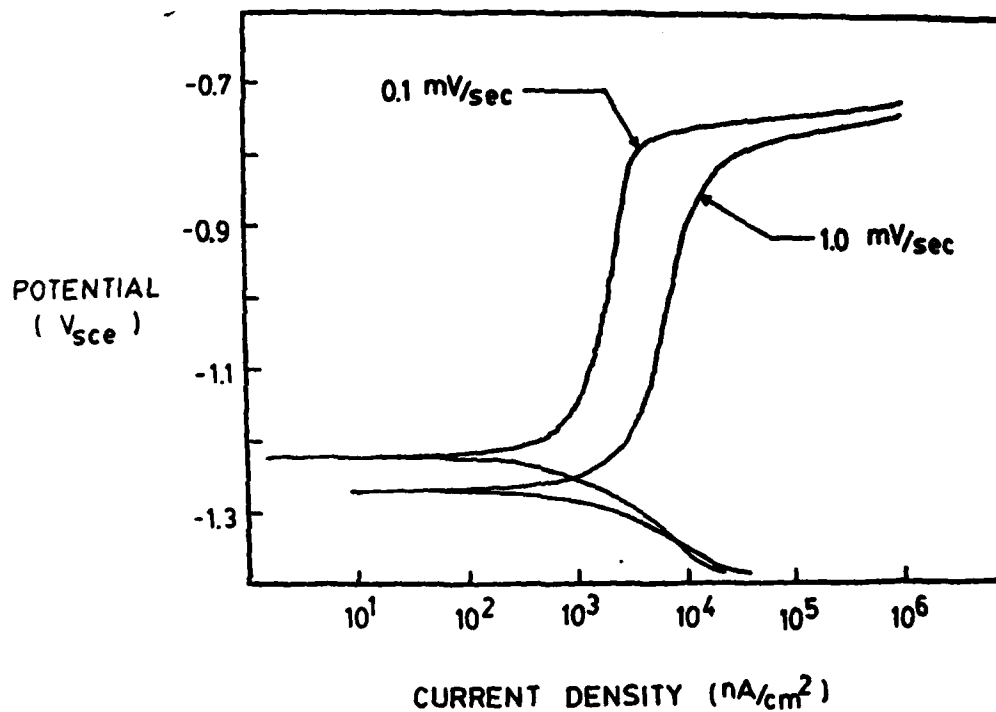


Figure 2. Effect of Potentiodynamic Scan Rate on the Polarization Behavior of the Al-Mg-Li Alloy in Deaerated 0.5 N Sodium Chloride at 23°C.

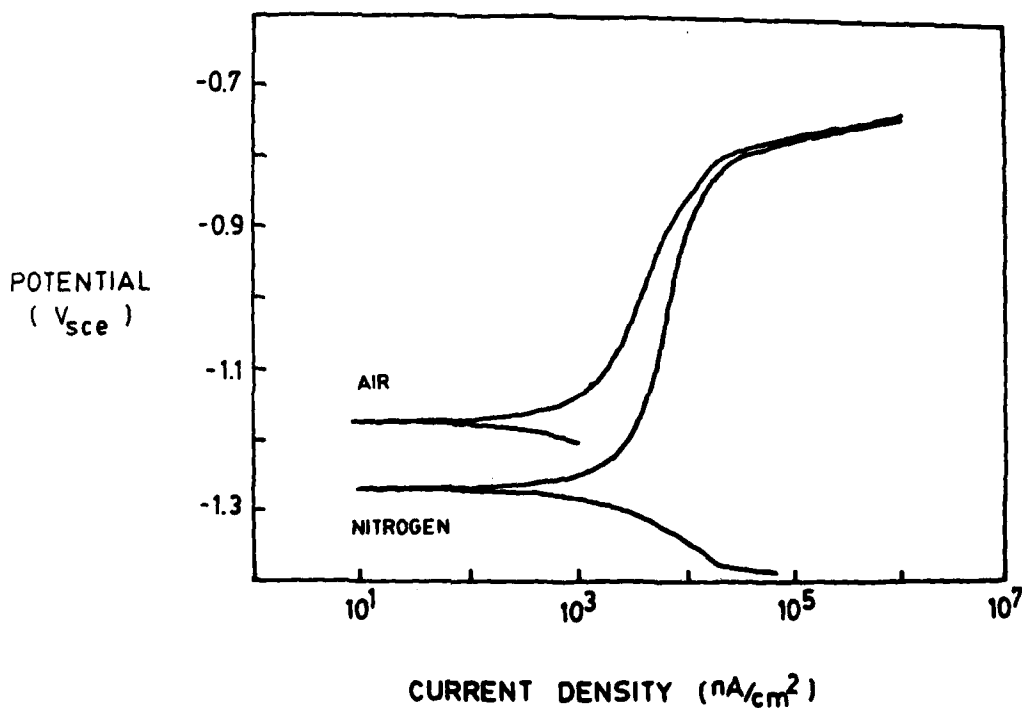


Figure 3. Effect of Solution Aeration on the Polarization Behavior of the Al-Mg-Li Alloy in 0.5 N Sodium Chloride at 23°C and 1 mV/sec scan rate.

Table II Effect of aeration and pH on the electrochemical behavior of aluminum alloy 7050 and an Al-Mg-Li alloy.

Alloy	Aeration	E_{corr}^1 (Vsce)	E_{pit}^2 (Vsce)	ΔE	I_{pass}^3 ($\mu A/cm^2$)
(a) pH=2, 0.5 N sodium chloride					
7050	Nitrogen	-0.745	-0.738	+	- - -
	Air	-0.724	-0.709	*	- - -
Al-Mg-Li	Nitrogen	-1.052	-0.770	0.282	110
	Air	-0.798	-0.766	0.032	18
(b) Neutral pH, 0.5 N sodium chloride					
7050	Nitrogen	-0.728	-0.699	0.029	- - -
	Air	-0.726	-0.708	*	- - -
Al-Mg-Li	Nitrogen	-1.236	-0.805	0.431	7.3
	Air	-1.160	-0.789	0.371	4.4
(c) pH=10, 0.5 N sodium chloride					
7050	Nitrogen	-1.240	-0.712	0.528	4.3
Al-Mg-Li	Nitrogen	-1.342	-0.795	0.547	20
	Air	-1.364	-0.782	0.582	33

+ Occasionally pitting occurs immediately on passing the zero potential during the scan.

* Pitting occurs immediately on passing the zero potential during the scan.

considerably different in neutral solutions and are closer again in aerated acidic solutions. Figure 4 shows the effect of varying the pH in 0.5 N sodium chloride solutions under deaerated and aerated conditions.

Temperature

Increasing the temperature reduces the free corrosion potential and the pitting potential while increasing the passive current density. Figure 5 shows the effect of temperature on the polarization behavior of the alloys. In this figure, it can be seen that altering the temperature affected the alloys similarly, but that the pitting potential of the 7050 alloy shifted more as a function of temperature. Figure 6 shows the open circuit corrosion potential and pitting potential versus temperature for the alloys.

Chloride Ion Concentration

Chloride ions or other ionic species in the environment can cause pitting of these as well as other alloys. Accordingly, the pitting potential of the alloys varies with the concentration or activity of the ionic species present. Figure 7 shows the effect of chloride ion concentration on the polarization behavior of the Al-Mg-Li alloy. In figure 8, the chloride ion activity is plotted against the pitting and corrosion potentials. For this figure, the activities were calculated from the concentrations using the activity coefficients of Latimer (7).

Discussion

Aeration

Increasing the oxygen content of the environment increases the oxygen in the passive film and increases the nobility of the sample. This reduces the corrosion rate, as indicated by the reduction in the passive current density, but it also increases the driving force for pitting. If the free corrosion potential reaches the critical pitting potential, pitting results. The 7050 alloy frequently pitted prior to initiation of a scan in aerated sodium chloride solutions. Since the free corrosion potential of the lithium containing alloy is more active, it did not pit in this situation.

pH

Aluminum oxides are soluble in both high and low pH solutions (2,8). As a result, either increasing the pH or decreasing the pH increases the corrosion rate of both alloys. Foley et. al. studied the relative behavior of several anions toward the oxides of aluminum and the passive film on aluminum surfaces (8,9). They concluded that while halides were very detrimental, the most aggressive anion was the hydroxide ion. However, pit initiation is apparently pH independent.

Temperature

Increasing the temperature decreased the pitting potentials. This means that the alloys are more resistant to

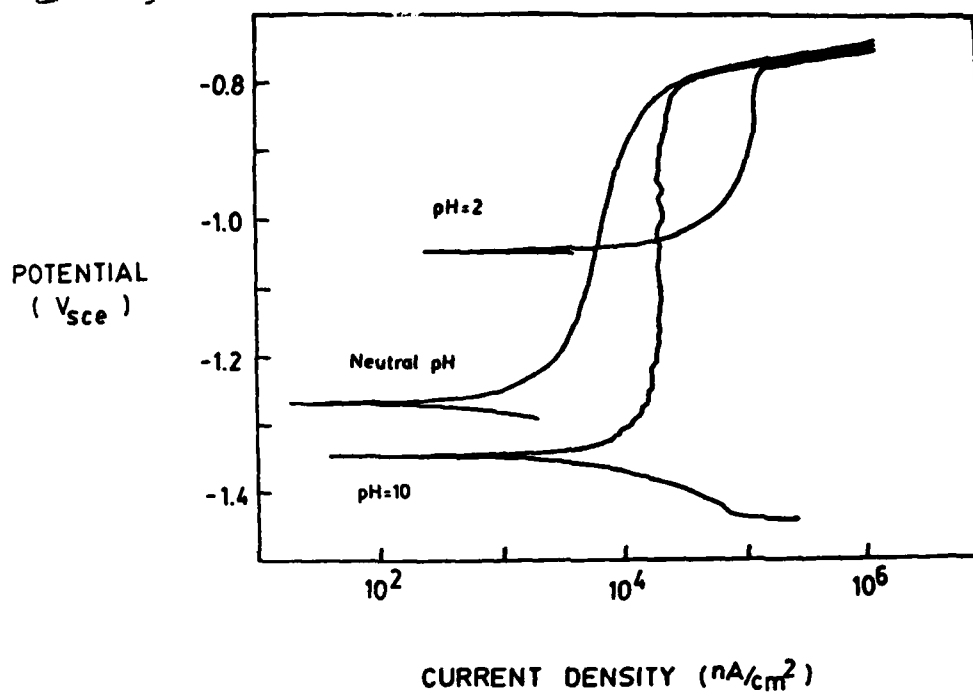


Figure 4A. Effect of pH on the Polarization Behavior of the Al-Mg-Li Alloy in Deaerated 0.5 N Sodium Chloride at 23°C and 1 mV/sec scan rate.

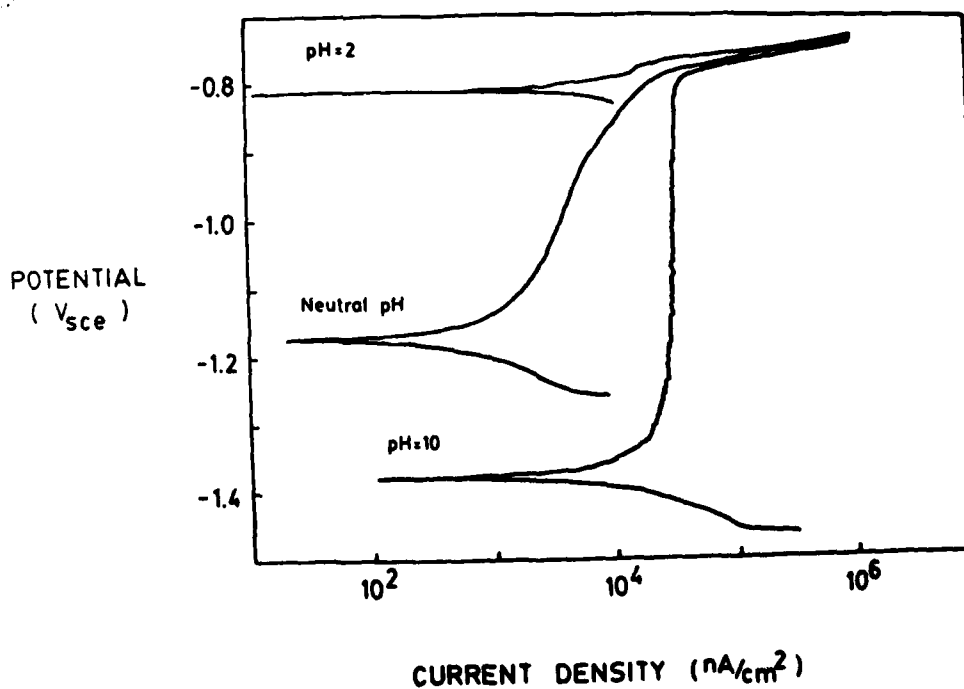


Figure 4B. Effect of pH on the Polarization Behavior of the Al-Mg-Li Alloy in Aerated 0.5 N Sodium Chloride at 23°C and 1 mV/sec scan rate.

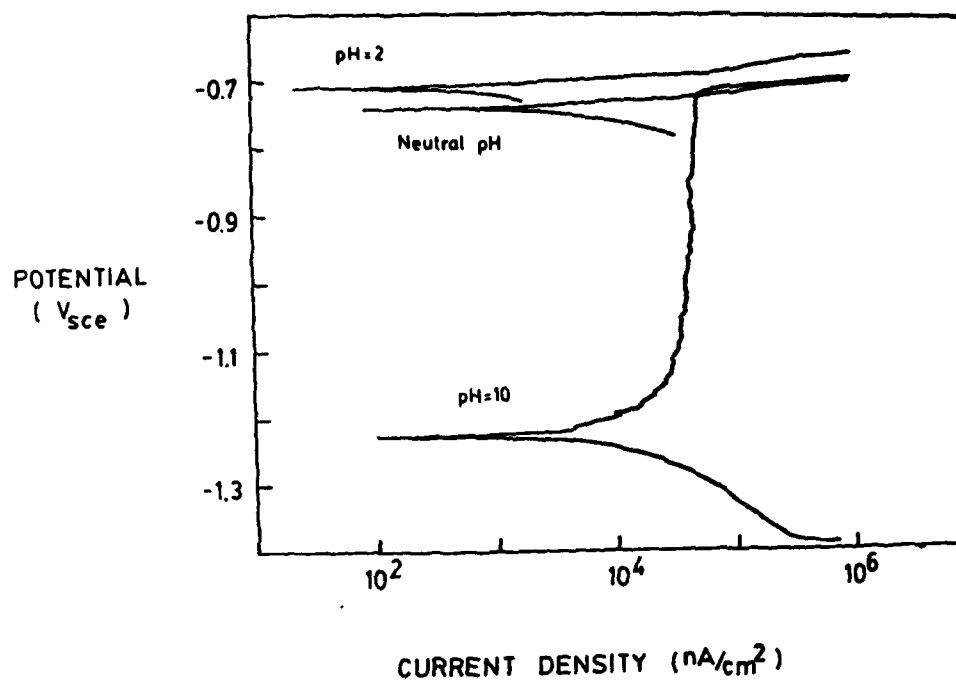


Figure 4C. Effect of pH on the Polarization Behavior of Alloy 7050 in Deaerated 0.5 N Sodium Chloride at 23°C and 1 mV/sec scan rate.

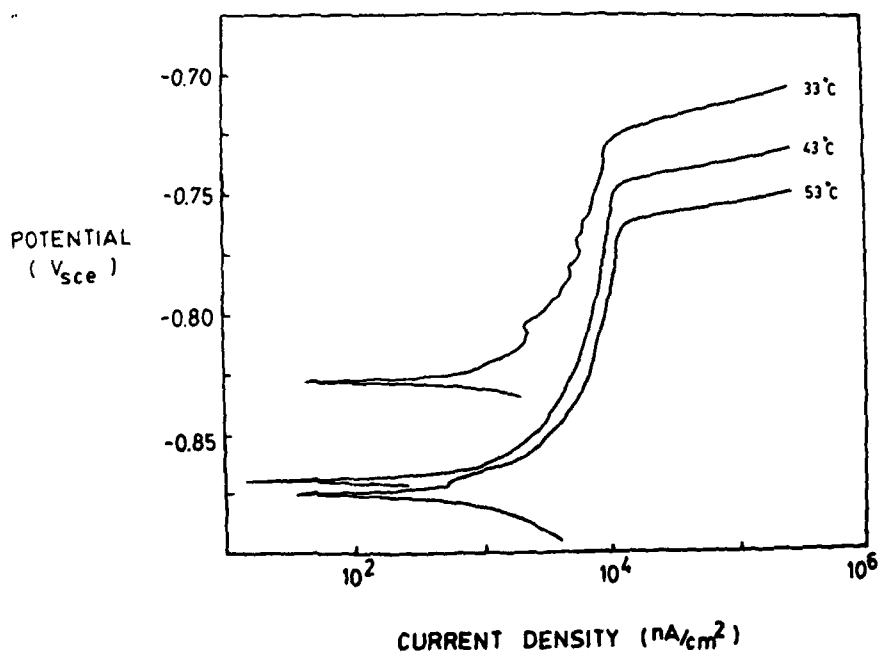


Figure 5A. Effect of Temperature on the Polarization Behavior of Alloy 7050 in Deaerated 0.5 N Sodium Chloride at 1 mV/sec scan rate.

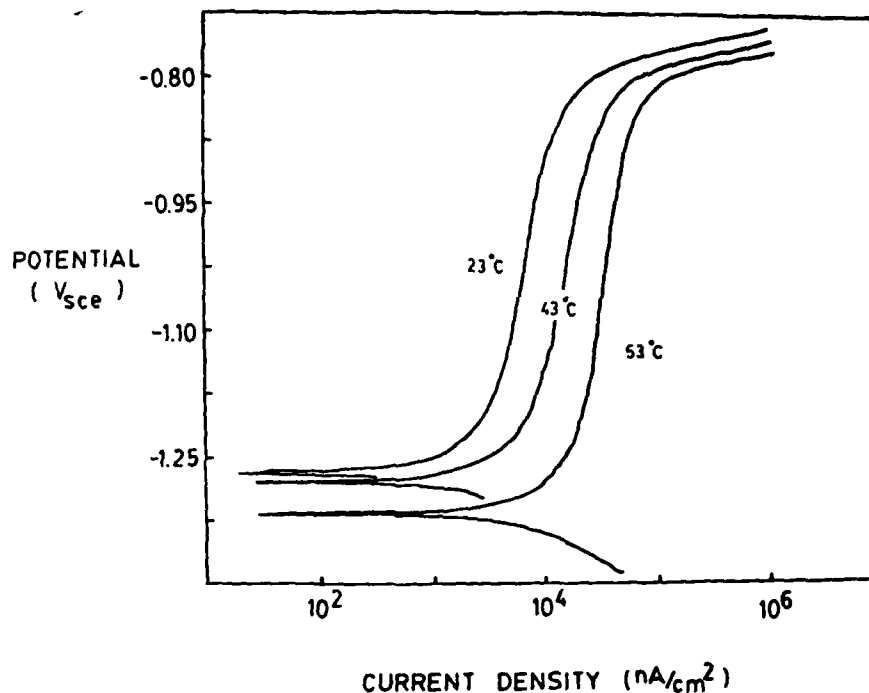


Figure 5B. Effect of Temperature on the Polarization Behavior of the Al-Mg-Li Alloy in Deaerated 0.5 N Sodium Chloride at 1 mV/sec scan rate.

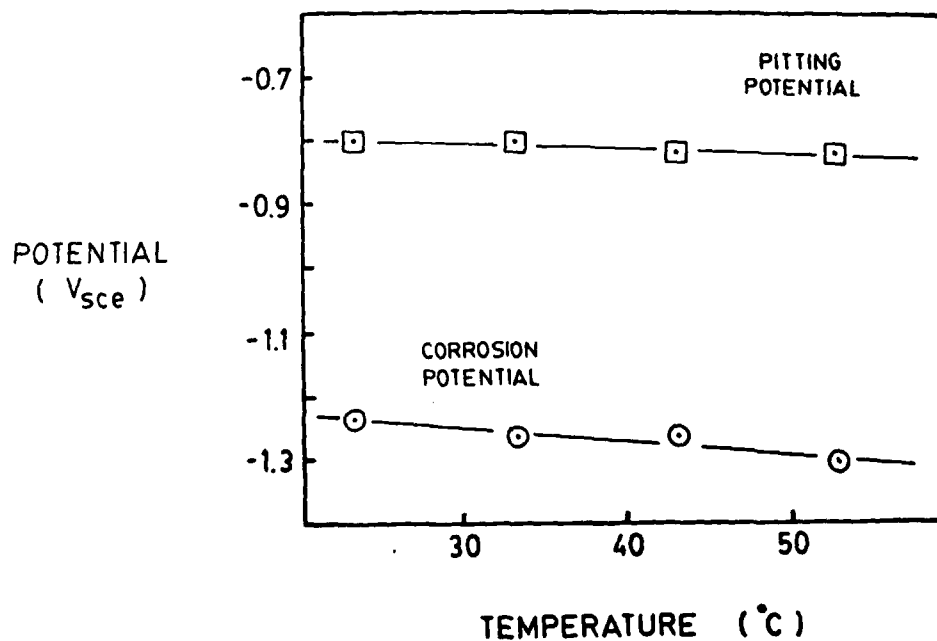


Figure 6A. Temperature versus the Corrosion and Pitting Potentials for the Al-Mg-Li Alloy in Deaerated 0.5 N Sodium Chloride.

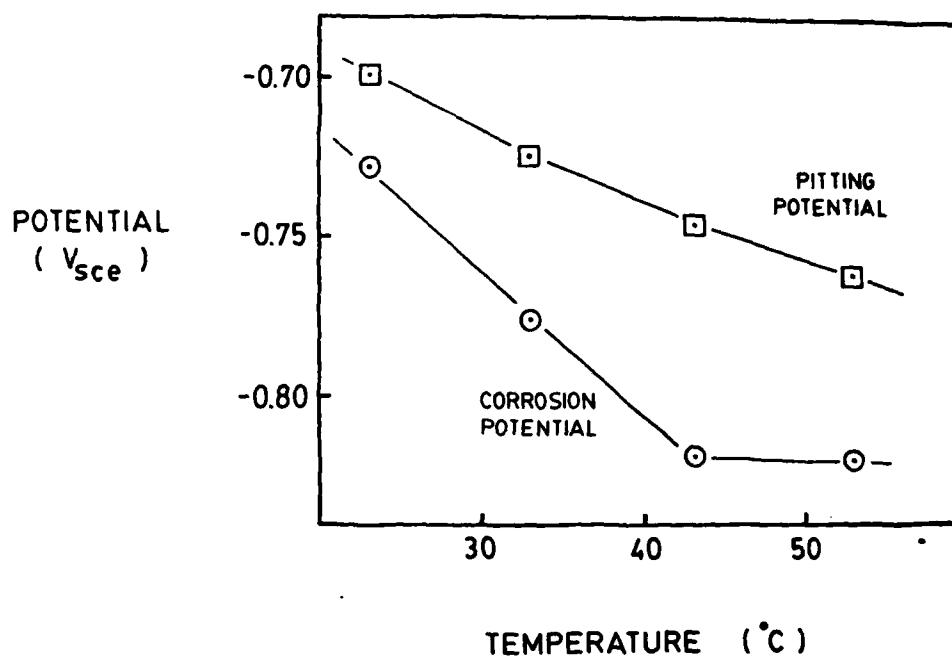


Figure 6B. Temperature versus the Corrosion and Pitting Potentials for Alloy 7050 in Deaerated 0.5 N Sodium Chloride.

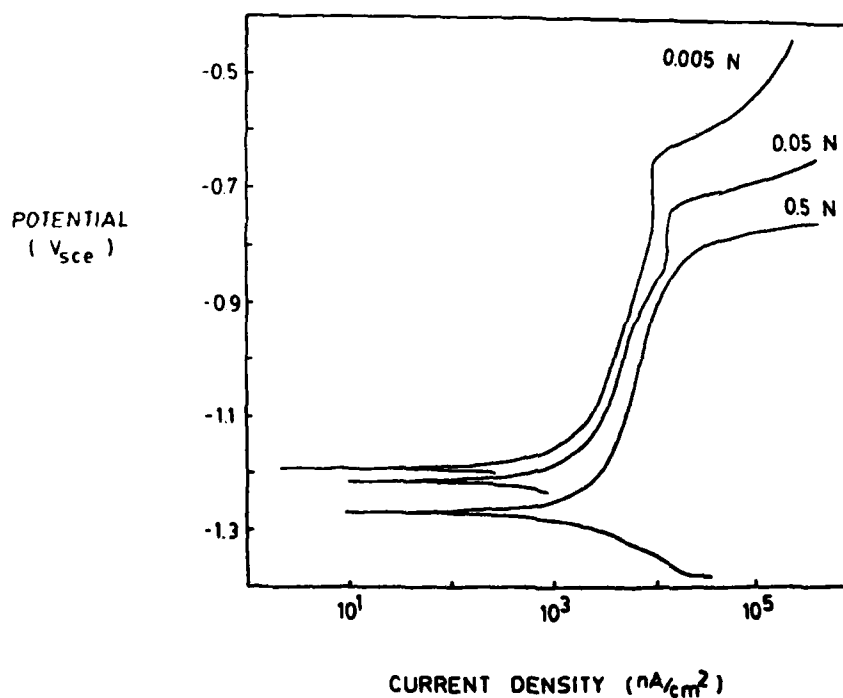


Figure 7A. Effect of Chloride Ion Concentration on the Polarization Behavior of the Al-Mg-Li Alloy in Deaerated Sodium Chloride at 23°C and 1 mV/sec scan rate.

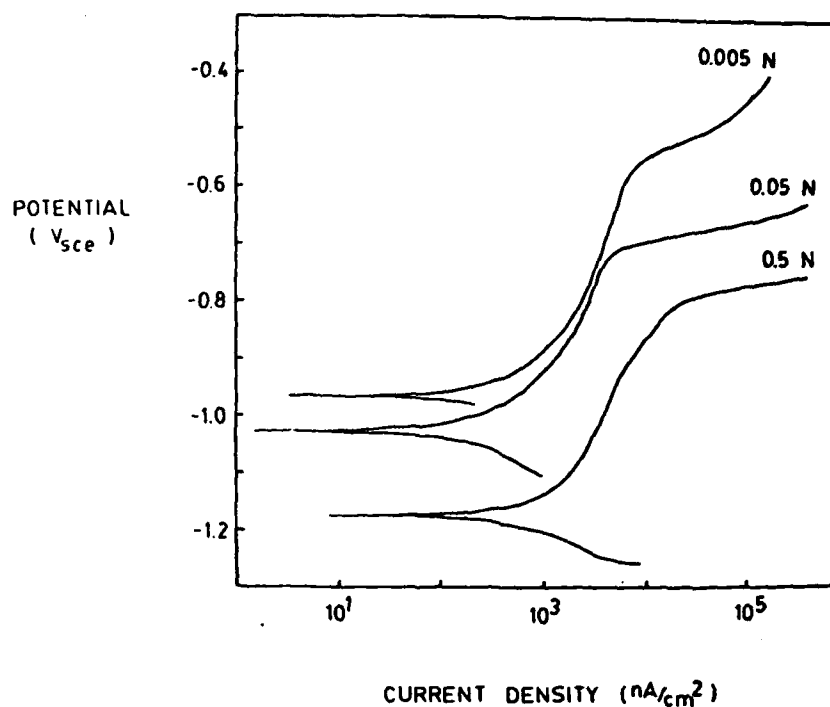


Figure 7B. Effect of Chloride Ion Concentration on the Polarization Behavior of the Al-Mg-Li Alloy in Aerated Sodium Chloride at 23°C and 1 mV/sec scan rate.

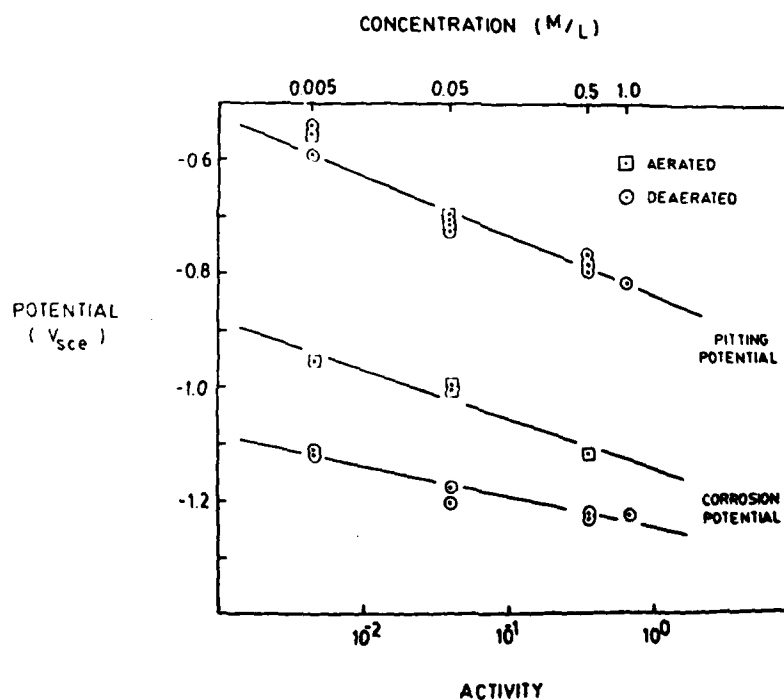


Figure 8. Chloride Ion Activity versus the Pitting and Corrosion Potentials of the Al-Mg-Li Alloy in Aerated and Deaerated Sodium Chloride Solutions at 23°C.

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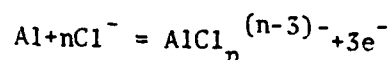
pitting at lower temperatures. Bohni and Uhlig (10) found little temperature effect on the pitting potentials of pure aluminum while other investigators report a similiar effect for pure aluminum to that reported here for the alloys (11,12). Bohni and Uhlig attributed the negligible temperature effect of aluminum to the absence of a temperature sensitive hydration and structure of the passive film. The observed potential shift with temperature of the 7050 is greater than for the Al-Mg-Li alloy. This suggests that either the scan rate-temperature dependence is different for the alloys or the temperature dependence of passive film hydration is different. It should be noted that the observed difference is in the range of reported differences by different investigators for pure aluminum (10-12).

Chloride Ion Concentration

The chloride ion concentration changes the pitting potential according to the relation:

$$E_p = E_p^0 + n\left(\frac{RT}{3F}\right) \ln[Cl^-]$$

Where "n" in the relationship is the stoichiometric factor or reaction order in the pitting reaction:



For the Al-Mg-Li alloy, the slope was found to be 106 mV/decade and the intercept was found to be at -843 mV. Stirrup et. al. found a slope of 100 mV/decade and an intercept of -757 mV for pure aluminum (11). Bohni and Uhlig found a slope of 124 mV/decade and an intercept of -746 mV for pure aluminum (10).

The more active intercept of the chloride activity vs. pitting potential line for the Al-Mg-Li alloy indicates that this alloy is more susceptible to pitting at all chloride concentrations than pure aluminum. Since the slopes for the alloy and pure aluminum are the same, then the pitting reaction is the same or of the same order. This indicates that the protective passive film on the lithium alloy is the same or at least similiar to the film on pure aluminum. The increased susceptibility to pitting may be due to either retardation of film repair kinetics or to an increase in the flaws in the film. This would also explain the shift in the free corrosion potential toward more active potentials.

Alloy Effect

For the Al-Mg-Li alloy compared to the 7050 alloy, the corrosion potential is usually more active and the pitting potential is also slightly less noble. Also, the passive current density at a given potential is higher. This indicates that the passive film on the lithium alloy is less protective.

The active shift in pitting potential indicates less resistance to pit initiation for the Al-Mg-Li alloy. The

difference between the intercept of the chloride ion activity verses pitting potential line, discussed above, for the Al-Mg-Li alloy and pure aluminum is about 100 mV. Thus, for a given electrochemical potential pits will initiate in the lithium alloy more readily than in pure aluminum or alloy 7050. However, the reduced free corrosion potential reduces the probability of pitting under free corrosion conditions. If the Al-Mg-Li alloy is galvanically coupled with either pure aluminum or alloy 7050, the Al-Mg-Li alloy would be expected to preferentially pit. The lithium in the alloy is not necessarily responsible for the shift in pitting potential. Bohni and Uhlig found that additions of either Mg or Mn shifted the pitting potential in the active direction for pure aluminum (10). Since the lithium alloy also contains more magnesium than the 7050 alloy, table I, the increased pitting susceptibility cannot be attributed to lithium alone.

The shift to more active corrosion potentials of lithium containing alloys has been shown to be primarily due to the addition of lithium, and results in increased free corrosion rates (3,4). However, the polarization behavior indicates that the free corrosion potentials are still in the passive regime and that the corrosion rates estimated from the curves are not significantly different compared to the accuracy of the techniques for estimating corrosion rates.

Conclusion

The corrosion behavior of the lithium containing alloy is different from that of alloy 7050. The Al-Mg-Li alloy is slightly more susceptible to pitting and general attack. The changes in pitting potential as a function of temperature and chloride ion activity are essentially the same as for pure aluminum. Therefore, the passive film protecting the lithium alloy at the pitting potential is essentially the same as the passive film on pure aluminum. The increased susceptibility may be due to either retardation of repassivation kinetics or due to imperfections in the passive layer.

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